SYNTHESIS OF CSSnI₃ BY A SOLUTION BASED METHOD

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ABSTRACT

This invention discloses a solution based synthesis of cesium tin tri-iodide (CsSnI₃). More specifically, the CsSnI₃ is fabricated in an organic Perovskite precursor solvent. CsSnI₃ are ideally suited for a wide range of applications such as light emitting and photovoltaic devices.

7 Claims, 2 Drawing Sheets
Figure 1
Figure 2
SYNTHESIS OF CSSnI₃ BY A SOLUTION BASED METHOD

BACKGROUND OF THE INVENTION

1. Field of the Invention
The invention generally relates to the formation of materials for photovoltaic devices and more specifically to the synthesis of CsSnI₃ by solution based method.

2. Description of the Prior Art
The current photovoltaic technologies can be classified by the different materials used for the light absorption in a solar cell. These materials include amorphous and polycrystalline silicon, CdTe, CuInGaSe₂ (CIGS), GaAs, and photosensitive organic dyes. A transformative technology may emerge when a new and better material is discovered for photovoltaic applications.

CsSnI₃ is a unique phase-change material that exhibits four polymorphs. The black polymorph of CsSnI₃ could be obtained through a phase transition from the yellow polymorph of CsSnI₃ by increasing its temperature above 425 K. It was further demonstrated by differential thermal analysis and X-ray diffraction that during the cooling of the black CsSnI₃ from 450 K, its ideal cubic Perovskite structure (B-α) deformed to a tetragonal structure (B-β) at 426 K, and became an orthorhombic structure (B-γ) below 351 K. [1] The CsSnI₃ is unique in combining two generally contra-indicated properties, strong photoluminescence (PL) and high electrical conductivity. [2, 3]

A need still exists in the industry for developing synthesis methods for CsSnI₃, especially in large scale. The successful implementation of these materials for various applications requires a detailed understanding of both their processing and materials properties.

At present, the synthesis of CsSnI₃ can be divided into solid-phase sintering and solution based methods. The solid-phase sintering method needs vacuum and high temperature which means high production costs. [1] For solution based method, K. Shum and Z. Chen offered a simple way to synthesize CsSnI₃, but the final product is not pure (U.S. Published Patent Application No. 2012/0306553). Here, we provide a simple solution based method to synthesize substantially pure CsSnI₃.

SUMMARY OF THE INVENTION

This invention is directed to synthesizing cesium tin triiodide (CsSnI₃) by a solution based method.

According to one aspect of the invention one embodiment in accordance with the invention is directed to a process of forming homogeneous CsSnI₃ in an organic Perovskite precursor solvent, comprising steps of:

1. forming CsI solution from CsI powder;
2. providing SnI₂;
3. adding the SnI₂ into the CsI solution to form a mixture wherein the molar ratio of the SnI₂ to CsI in the mixture is approximately 1:1;
4. heating the mixed solution at a temperature within the range of 50°C to 250°C until all the solvent is evaporated to form CsSnI₃ powder, and
5. the process steps (1) to (4) are performed in a substantially inert environment.

The substantially inert environment may be created within a glove box and comprises a protective gas, such as N₂, including water vapor and oxygen content both under 1 ppm and the temperature while heating the mixed solution ranges from about 50°C to 250°C.

The homogeneous CsSnI₃ is formed by adding a SnI₂ solution into a CsI solution to form a mixture, and stirring the mixture for 1 to 3 hours to ensure that the raw materials have fully reacted, and then the solution is aged for 12 to 24 hours to form the homogeneous CsSnI₃ precursor solution.

The CsI solution is about 25 mmol/L to 2 mol/L CsI solution by fully dissolving CsI powder (99.999% purity) in a solvent, and the SnI₂ solution is about 25 mmol/L to 2 mol/L SnI₂ solution by fully dissolving SnI₂ powder (99% purity) in a solvent.

The solvent for dissolving CsI powder (99.999% purity) is selected to serve as a Perovskite ligand to form coordination complexes, such as N,N-dimethylformamide (DMF), γ-butyrolactone (GBL) and mixtures thereof.

In the aforementioned process the SnI₂ is in the form of a SnI₂ solution.

The solvent for dissolving SnI₂ powder (99.999% purity) is selected to serve as a Perovskite ligand to form coordination complexes, such as N,N-dimethylformamide (DMF), γ-butyrolactone (GBL) and mixtures thereof.

The SnI₂ is in the form of a powder.

Other halides may be used to practice the invention. For example, a process of forming homogeneous CsSnI₃₋ₓXₓ in an organic Perovskite precursor solvent, comprises the steps of:

1. forming CsI solution from CsI powder;
2. providing SnI₂ and SnX₂;
3. adding the SnI₂ and SnX₂ into the CsI solution to form a mixture wherein the molar ratio of the raw materials is SnX₂:SnI₂:CsI = y:1:1, where 0≤x≤1;
4. heating the final mixed solution at a temperature within the range of 50°C to 250°C until all the solvent is evaporated to form CsSnI₃₋ₓXₓ wherein X is a halogen element selected from Group VIIA of the periodic table consisting of fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At) and 0≤x≤3; and
      the process steps (1) to (4) are performed in a substantially inert environment.

In the aforementioned process the substantially inert environment may be created within a glove box and comprises a protective gas, such as N₂, including water vapor and oxygen content both under 1 ppm and the temperature while heating the final mixed solution ranges from about 50°C to 250°C.

The homogeneous CsSnI₃₋ₓXₓ is formed by adding a mixed solution of SnI₂ and SnX₂ into a CsI solution to form a mixture, and stirring the mixture for 1 to 3 hours to ensure that the raw materials have fully reacted, and then the solution is aged for 12 to 24 hours to form the homogeneous CsSnI₃₋ₓXₓ precursor solution.

The CsI solution is about 25 mmol/L to 2 mol/L CsI solution by fully dissolving CsI powder (99.999% purity) in a solvent, and the mixed solution of SnI₂ and SnX₂ is about 25 mmol/L to 2 mol/L by fully dissolving SnI₂ and SnX₂ powder (99% purity) in a solvent.

The solvent for dissolving CsI powder (99.999% purity) is selected to serve as a Perovskite ligand to form coordination complexes, such as N,N-dimethylformamide (DMF), γ-butyrolactone (GBL) and mixtures thereof.

The SnI₂ and SnX₂ are in the form of a SnI₂ and SnX₂ solution.

The solvent for dissolving the SnI₂ and SnX₂ powder (99.999% purity) is selected to serve as a Perovskite ligand to form coordination complexes, such as N,N-dimethylformamide (DMF), γ-butyrolactone (GBL) and mixtures thereof.
The SnI and SnX are in the form of a powder. In the process, the steps are preferably performed in a glove box under the protection of N₂ gas and the molar ratio of the SnI₂ and CsI in the mixture is essentially 1:1.

The CsI solution is made by fully dissolving CsI powder (99.999% purity) in a solvent selected from the Perovskite precursor solutions, such as N,N-dimethylformamide (DMF), γ-butyrolactone (GBL) and mixtures thereof. The concentration of CsI solution is about 25 mmol/L to 500 mmol/L.

The SnI₂ solution is made by fully dissolving SnI₂ powder (99% purity) in a solvent selected from the Perovskite precursor solutions, such as N,N-dimethylformamide (DMF), γ-butyrolactone (GBL) and mixtures thereof. The concentration of SnI₂ solution is about 25 mmol/L to 500 mmol/L.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are incorporated in and form a part of the specification, illustrate preferred embodiments of the present invention, and together with the description, serve to explain the principles of the invention, in which:

FIG. 1 shows the schematic diagram for the synthesis of CsSnI₃; and
FIG. 2 shows the (a) X-ray diffraction data (XRD) profile taken from CsSnI₃ (concentrations of CsI and SnI₂ were both 50 mmol/L) and (b) standard XRD pdf card (43-1162) of black-γ phase of CsSnI₃.

DETAILED DESCRIPTION AND EXAMPLES

The CsSnI₃ exhibits outstanding optical, electrical, and ferroelectric properties. These features make CsSnI₃ ideally suited for a wide range of applications such as light emitting and photovoltaic devices.

More specifically, CsSnI₃ is a promising material in the application of solar cells since CsSnI₃ was found to possess a direct band gap of 1.32 eV at room temperature, right in the narrow region of optimal band gaps for the Shockley-Queisser maximum efficiency limit of a solar cell.

An effective method to synthesize large domain size high quality Perovskite semiconductor according to the present invention is disclosed. More specifically, a solution based method to synthesize CsSnI₃ is disclosed according to the present invention. The CsSnI₃ can be fabricated in an organic Perovskite precursor solvent as shown in FIG. 1. This synthesis method of the CsSnI₃ further enhances the likelihood of using CsSnI₃ as a new absorption material for solar cells.

Examples of procedures for synthesizing polycrystalline CsSnI₃ using reaction raw materials are described below. Generally, a process of forming homogeneous CsSnI₃ in an organic Perovskite precursor solvent, comprises the steps of:

(1) forming CsI solution from CsI powder;

(2) providing SnI₂;

(3) adding the SnI₂ into the CsI solution to form a mixture wherein the molar ratio of the SnI₂ and CsI in the mixture is substantially 1:1;

(4) heating the mixed solution at a temperature within the range of 50°C to 250°C, until all the solvent is evaporated to form CsSnI₃ powder, and

the process steps (1) to (4) are performed in a substantially inert environment.

The substantially inert environment may be created within a glove box and comprises a protective gas, such as N₂, including water vapor and oxygen content both under 1 ppm and the temperature while heating the mixed solution ranges from about 50°C to 250°C.

The homogeneous CsSnI₃ is formed by adding a SnI₂ solution into a CsI solution to form a mixture, and stirring the mixture for 1 to 3 hours to ensure that the raw materials have fully reacted, and then the solution is aged for 12 to 24 hours to form the homogeneous CsSnI₃ precursor solution.

The CsI solution is about 25 mmol/L to 2 mol/L CsI solution by fully dissolving CsI powder (99.999% purity) in a solvent, and the SnI₂ solution is about 25 mmol/L to 2 mol/L SnI₂ solution by fully dissolving SnI₂ powder (99% purity) in a solvent.

The solvent for dissolving CsI powder (99.999% purity) is selected to serve as a Perovskite ligand to form coordination complexes, such as N,N-dimethylformamide (DMF), γ-butyrolactone (GBL) and mixtures thereof.

The SnI₂ is in the form of a SnI₂ solution. The solvent for dissolving SnI₂ powder (99% purity) is selected to serve as a Perovskite ligand to form coordination complexes, such as N,N-dimethylformamide (DMF), γ-butyrolactone (GBL) and mixtures thereof.

The CsSnI₃ is in the form of a CsSnI₃ solution. The solvent for dissolving CsSnI₃ powder (99.999% purity) is selected to serve as a Perovskite ligand to form coordination complexes, such as N,N-dimethylformamide (DMF), γ-butyrolactone (GBL) and mixtures thereof.

The SnX₃ is in the form of a SnX₃ solution. Other halides may be used to practice the invention. More generally, a process of forming homogeneous CsSnI₃-X₃ in an organic Perovskite precursor solvent, comprises steps of:

(1) forming CsI solution from CsI powder;

(2) providing SnI₂ and SnX₂;

(3) adding the SnI₂ and SnX₂ into the CsI solution to form a mixture wherein the molar ratio of the raw materials is SnX₂:SnI₂:CsI=y:z:(1-y):1, where 0≤y≤1;

(4) heating the final mixed solution at a temperature within the range of 50°C to 250°C, until all the solvent is evaporated to form CsSnI₃-X₃, wherein X is a halogen element selected from Group VIIA of the periodic table consisting of fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At) and 0≤x≤3; and

the process steps (1) to (4) are performed in a substantially inert environment.

The substantially inert environment may be created within a glove box and comprises a protective gas, such as N₂, including water vapor and oxygen content both under 1 ppm and the temperature while heating the mixed solution ranges from about 50°C to 250°C.

The homogeneous CsSnI₃-X₃ is formed by adding a mixed solution of SnI₂ and SnX₂ into a CsI solution to form a mixture, and stirring the mixture for 1 to 3 hours to ensure that the raw materials fully reacted, and then the solution is aged for 12 to 24 hours to form the homogeneous CsSnI₃-X₃ precursor solution.

The CsI solution is about 25 mmol/L to 2 mol/L CsI solution by fully dissolving CsI powder (99.999% purity) in a solvent, and the mixed solution of SnI₂ and SnX₂ is about 25 mmol/L to 2 mol/L by fully dissolving SnI₂ and SnX₂ powder (99% purity) in a solvent.

The solvent for dissolving CsI powder (99.999% purity) is selected to serve as Perovskite ligand to form coordination complexes, such as N,N-dimethylformamide (DMF), γ-butyrolactone (GBL) and mixtures thereof.

The SnI₂ and SnX₂ are in the form of a SnI₂ and SnX₂ solution.

The solvent for dissolving the SnI₂ and SnX₂ powder (99.999% purity) is selected to serve as a Perovskite ligand to form coordination complexes, such as N,N-dimethylformamide (DMF), γ-butyrolactone (GBL) and mixtures thereof.
The SnI and SnX are in the form of a powder. The procedures of synthesizing polycrystalline CsSnI₃ using reaction raw materials have been described.

The reaction raw materials were milled and dissolved in a glove box under protect of N₂ gas. The conditions in the glove box were: room temperature or temperature of 298.15 K (or 25°C), 77% H₂ water vapor and oxygen content are both under 1 ppm; and an absolute pressure of 100 kPa (or 14.504 psi, 0.986 atm).

WORKING EXAMPLES

Example 1

Preparation of CsI Solution

Initially, 0.13 gram of CsI (99.999% purity) powder was added to 10 ml GBL. The CsI powder was fully dissolved in GBL. The CsI solution was stirred for 30 minutes. CsI solution was colorless and stable in glove box. It would be apparent to one skilled in the art that CsI solutions could be made using any solvents in addition to those used in the examples. Examples of solvents that can be used include but are not limited to N,N-dimethylformamide (DMF), γ-butyrolactone (GBL) and mixtures thereof.

The concentration range of the CsI solution was from about 25 mmol/L to 500 mmol/L.

Example 2

Preparation of SnI₂ Solution

Initially, 0.186 gram of SnI₂ (99% purity) powder was added to 10 ml GBL. The SnI₂ powder was fully dissolved in GBL. The SnI₂ solution was stirred for 30 minutes. SnI₂ solution was yellow and stable in glove box. It would be apparent to one skilled in the art that SnI₂ solutions could be made using any solvents in addition to those used in the examples. Examples of solvents that can be used include but are not limited to, DMF, GBL or mixtures thereof.

The concentration range of the SnI₂ solution was from about 25 mmol/L to 500 mmol/L.

Example 3

Synthesis of CsSnI₃

A given amount of the prepared CsI solution was transferred to a reaction vial first. SnI₂ solution was then slowly added into the vial. The concentrations range of CsI and SnI₂ were both in a range of 25 mmol/L to 500 mmol/L, and their molar ratio was 1:1.

The mixed solution was stirred for 12 to 24 hours, and a uniform and transparent yellow CsSnI₃ solution was formed. The homogeneous CsSnI₃ solution was dried until the solvent was all evaporated. The heating temperature ranged from about 100°C to 200°C. Then the pure black CsSnI₃ powder with metallic luster was obtained as shown in FIG. 1. The chemical reaction for the mixed solution could be described as the following:

\[
\text{CsI + SnI}_2 \rightarrow \text{CsSnI}_3
\]

The reaction was verified by identifying the end products of CsSnI₃ using the X-ray diffraction (XRD) data.

FIG. 2 (a) shows the XRD data profile taken from CsSnI₃ (concentrations of CsI and SnI₂ were both 50 mmol/L).

FIG. 2 (b) showed the standard XRD pdf card (43-1162) of black-γ phase of CsSnI₃. All the measured peaks were well matched to the black-γ phase of CsSnI₃.

In summary, CsSnI₃ was synthesized using the CsI and SnI₂ by solution based method. A solution based method, was employed to fabricate CsSnI₃, especially suitable for solar cell applications. The polycrystalline quality was characterized by XRD data.

While the invention has been described in detail and with reference to specific examples thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

APPENDIX


What is claimed is:

1. A process of forming CsSnI₃ powder, comprising the steps of:
   (a) forming a CsI solution by dissolving CsI powder of purity equal to 99.999% in an organic solvent consisting of at least one of N,N-dimethylformamide (DMF), γ-butyrolactone (GBL) and mixtures thereof;
   (b) forming a SnI₂ solution by dissolving SnI₂ powder of purity equal to 99% in an organic solvent consisting of at least one of N,N-dimethylformamide (DMF), γ-butyrolactone (GBL) and mixtures thereof;
   (c) adding the SnI₂ solution into the CsI solution to form a composite solution wherein the molar ratio of the SnI₂ and CsI in said composite solution is approximately 1:1;
   (d) stirring said composite solution for at least one hour to obtain a homogeneous CsSnI₃ precursor solution;
   (e) aging said precursor solution at least for a predetermined time period after said stirring step;
   (f) heating said precursor solution following said aging step at a temperature within the range of 50°C to 250°C until all the solvent is evaporated to form CsSnI₃ powder exhibiting an XRD diffraction peak pattern for CsSnI₃ corresponding to the standard XRD-PDF card (43-1162) for the B-γamma-CsSnI₃ phase without exhibiting an XRD diffraction peak pattern for CsSnI₃;
   (g) the process steps (a) to (f) are performed in a substantially inert environment including a protective gas and water vapor and oxygen each at a level below 1 ppm.
2. The process of claim 1, wherein said substantially inert environment is created within a glove box.
3. The process of claim 1, wherein said precursor solution is aged for 12 to 24 hours to form a homogeneous CsSnI₃ precursor solution.
4. The process of claim 3, wherein said CsI solution is about 25 mmol/L to 2 mol/L CsI solution and the SnI₂ solution is about 25 mmol/L to 2 mol/L SnI₂ solution.
5. The process of claim 1, wherein said CsI powder is dissolved in said organic solvent to form CsI coordination complexes.
6. The process of claim 1, wherein said SnI$_2$ powder is dissolved in a said organic solvent to form SnI$_2$ coordination complexes.

7. The process of claim 2, wherein said protective gas is N$_2$. 